STUDY OF DIFFUSE X-RAY REFLECTION BY A SINGLE CRYSTAL OF META AMINOPHENOL*

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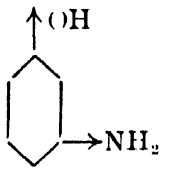
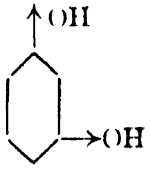
Plates XIV A-B

ABSTRACT. The refractive indices in different directions of the crystal were measured, the plane of molecule was taken to be in a perpendicular direction of least refractive index, namely in the *c*-direction The axes of the crystal were found, by rotation photographs, to be : $a=6.310$ A.U., $b=11.12$ A.U. and $c=8.60$ A.U. Planes (211), (330), (213), (212), (340), (321) (350), and (333) show extra Laue reflections, of which the extra Laue reflections from (211) persist from 18′ to 6.8′ and yield an interesting result when plotted on reciprocal lattice, namely, the derangement waves pass strictly on *b* axis)

Robertson has studied the structure of α-resorcinol ortho-$C_6H_4(OH)_2$. He has found that the structure of the crystal is fairly dense, since the hydrogen bonds draw the molecules closer together than the normal Van der Waals distance, and it is relatively isotropic. Lonsdale (1942) has found the most interesting results of diffuse X-ray reflection by resorcinol. The most noticeable features of the diffuse scattering are the dense halo surrounding the central spot, and the arrangement of diffuse spots on layer line. Since meta aminophenol has the similar structural formula as resorcinol, so it will be interesting to study X-ray properties as well as the optical properties of this crystal.



Meta aminophenol



Resorcinol

From early days of science the physicists and mineralogists have studied the optical properties of the crystals, because such studies gave some information about the structure of crystal. In the case of aromatic organic crystals, the refractive indices in different directions give the indications of the orientations of the benzene rings inside the crystals (Datta, 1947).

The crystal studied in the present Investigation was meta aminophenol. The substance was crystallised by slow evaporation of alcohol solution. The face

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angles of the crystal were measured and the axes were determined. The crystal belongs to orthrohombic system, hence the crystallographic directions are also the principal directions. The crystal was mounted on Fedorov stage placed between the crossed nicols of a polarising microscope, and the crystal was rotated about the direction until the extinction was observed. For the determination of the principal refractive indices, the Becke method was used. The crystal was immersed in a drop of liquid whose refractive index was intermediate between two principal indices of the crystal. The crystal was illuminated by polarised light and was rotated about the axis of the optical system until the Becke line disappeared. This was repeated for another liquid of intermediate refractive index. The two principal refractive indices α and β are given by the relations

$$\alpha^2 = \frac{n_1^2 n_2^2 \cos^2\theta_2 . \sin^2\theta_1 - n_1^2 n_2^2 \sin^2\theta_2 \cos^2\theta_1}{n_1^2 \sin^2\theta_1 - n_2^2 \sin^2\theta_2} \quad \ldots (1)$$

$$\beta^2 = \frac{n_1^2 n_2^2 \cos^2\theta_1 \sin^2\theta_2 - n_1^2 n_2^2 \sin^2\theta_2 \cos^2\theta_1}{n_1^2 \cos^2\theta_1 - n_2^2 \cos^2\theta_2} \quad \ldots (2)$$

where n_1 and n_2 are the refractive indices of the liquids and θ_1 and θ_2 are the angles between the first principal axis and the directions of electric vectors for the disappearance of the Becke line.

The third refractive index γ is obtained from the relation

$$\frac{\gamma}{\alpha}\sqrt{\frac{\alpha^2-\beta^2}{\beta^2-\gamma^2}} = \tan V_a$$

where V_a is half the optic-axial angle. The optic-axial angle was measured by the following method :

Both the analyser and polariser were moved simultaneously through 45 degrees. The hemisphere on the Fedorov stage was rotated on the horizontal circle until the extinction was obtained. This is half optic-axial angle.

Measurement on semi-optic-axial angle ($V_a = 15.30'$).—The measurement shows (010) plane to be optic-axial plane, with *a*-axis to be acute-besectrix, so that the crystal shows negative birefringes.

Measurement of α *and* γ.—The first liquid used has refractive index $= 1.552$ and extinction angle $= 53°$. The second liquid used has refractive index $= 1.515$ and extinction angle $= 74°$, Therefore, from

$$\alpha^2 = \frac{n_1^2 n_2^2 \cos^2\theta_2 \sin^2\theta_1 - n_1^2 n_2^2 \sin^2\theta_2 . \cos^2\theta_1}{n_1^2 \sin^2\theta_1 - n_2^2 \sin^2\theta_2}$$

we get $\alpha = 1.638$

and from $$\gamma^2 = \frac{n_1^2 n_2^2 \cos^2\theta_1 \sin^2\theta_2 - n_1^2 n_2^2 \cos^2\theta_2 . \sin^2\theta_1}{n_1^2 \cos^2\theta_1 - n_2^2 \cos^2\theta_2}$$

we get $\gamma = 1.505$.

From

$$\tan V_{\vec{a}} = \frac{\gamma}{\alpha}\sqrt{\frac{\alpha^2-\beta^2}{\beta^2-\gamma^2}}$$

$$\beta = \frac{\gamma\alpha.\ \sec V}{\sqrt{\gamma^2+\alpha^2\tan^2 V}} = 1.625.$$

Thus we haved $\alpha=1.638$, $\beta=1.625$ and $\gamma=1.505$. α, β and γ represent the refractive indices along a, b and c axes respectively.

The results show that the plane of benzene ring is closer to α and β directions than to γ direction.

α-resorcinol is relatively isotropic because OH bonds draw the molecules closer than the normal Van der Waals distance. In the case of meta amino-phenol one of OH is replaced by NH_2, which causes the higher anisotropy property of the crystals (Lonsdale and Smith, 1942).

We have studied X-ray properties of the crystal. The crystal is of orthorhombic-pyramidal type of pronounced hemimorphism with axial data, $a=6.310$ A.U., $b=11.12$ A.U., $c=8.60$ A.U. The number of molecules per unit cell is four and space group is C_{2v}^4 and simple lattice T_0 (Caspari, 1926).

The crystal shows extra Laue reflection when exposed to Ni-radiations. The planes (211), (330), (212), (213), (340), (321) and (333) show extra spots. One of the extra spots (211) shows very interesting results when plotted on reciprocal lattice network with values of a^* and b^* where $a^*=\lambda/a$ and $b^*=\lambda/b$. Let us consider a sphere that touches the orgin of the lattice and that has a unit radius. Any crystal plane will be in reflecting condition if the corresponding reciprocal lattice point lies on the surface of this sphere provided that the direction of incident X-ray beam is along the diameter of the sphere (Banerjee, 1947).

Figure 1 represents a set of crystal planes having the reciprocal lattice point at P and incident beam along OQ, The sphere of reflection is drawn with QO as its diameter, the distance QO being twice the distance that has been chosen as the unit distance for plotting the reciprocal lattice. The point P will be on the sphere of reflection if $\sin\theta=\rho/2$

On substitutig the value of ρ it will be equivalent to Bragg's equation, $\sin\theta=\lambda/2d$. The reflected ray will emerge out from crystal at an angle 2θ from the incident beam (Banerjee and Bose, 1944).

For equatorial layer line, the sphere of reflection will cut the reciprocal lattice network in a circle of unit radius and if X-ray passes along b^* axis of the crystal, the circle of unit radius is to be so placed that the diameter of the circle will be on b^* axis of the network. Then with centre O (origin of net work) and radius$=\xi$, we draw an arc which will cut the circle ($r_0=1$) at the point P, then co-ordinates of the point P will give the values of h and k. Now if the crystal is rotated through an angle ω on reciprocal lattice network through the origin O, the point O will remain the same as before,

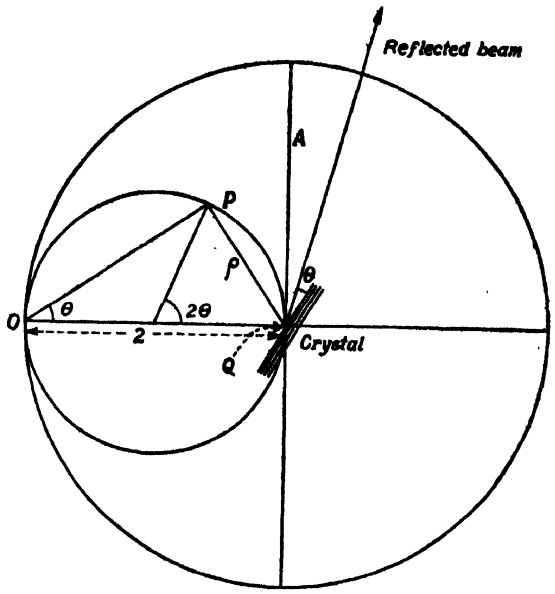


FIG. 1

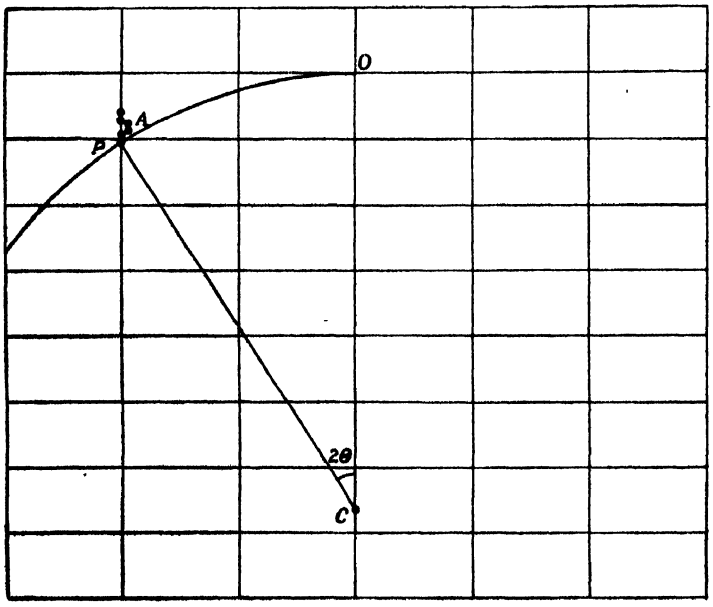
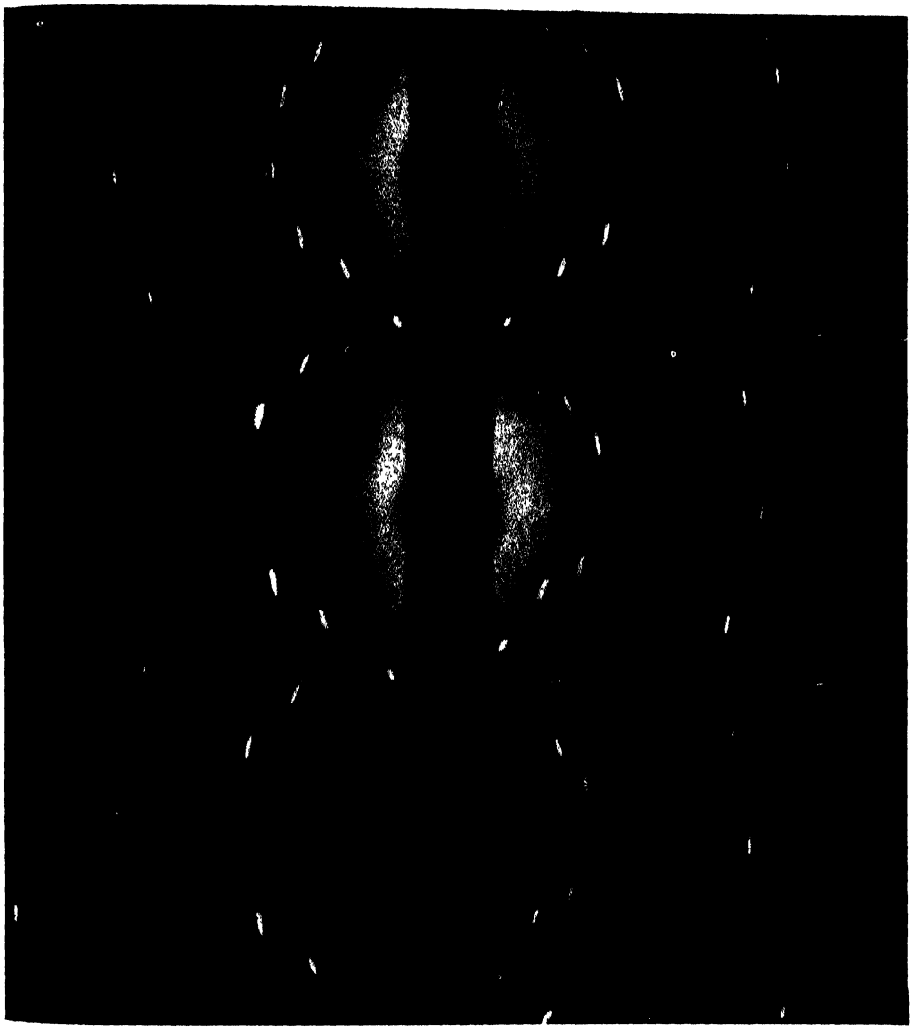


FIG. 2

Representation of extra spot (211) on a reciprocal lattice net work of a^* and b^*.
OC and CP are the directions of incident and scattered beam. A = positions of extra spots, 2θ = Bragg angle.

only the point Q will move to Q', so that QOQ' = angle of rotation. For any other layer n the sphere will cut the reciprocal lattice network in a smaller circle of radius r_n which is given by

$$r_n = \sqrt{r_0^2 - k_n^2 b^{*2}}$$



a

b

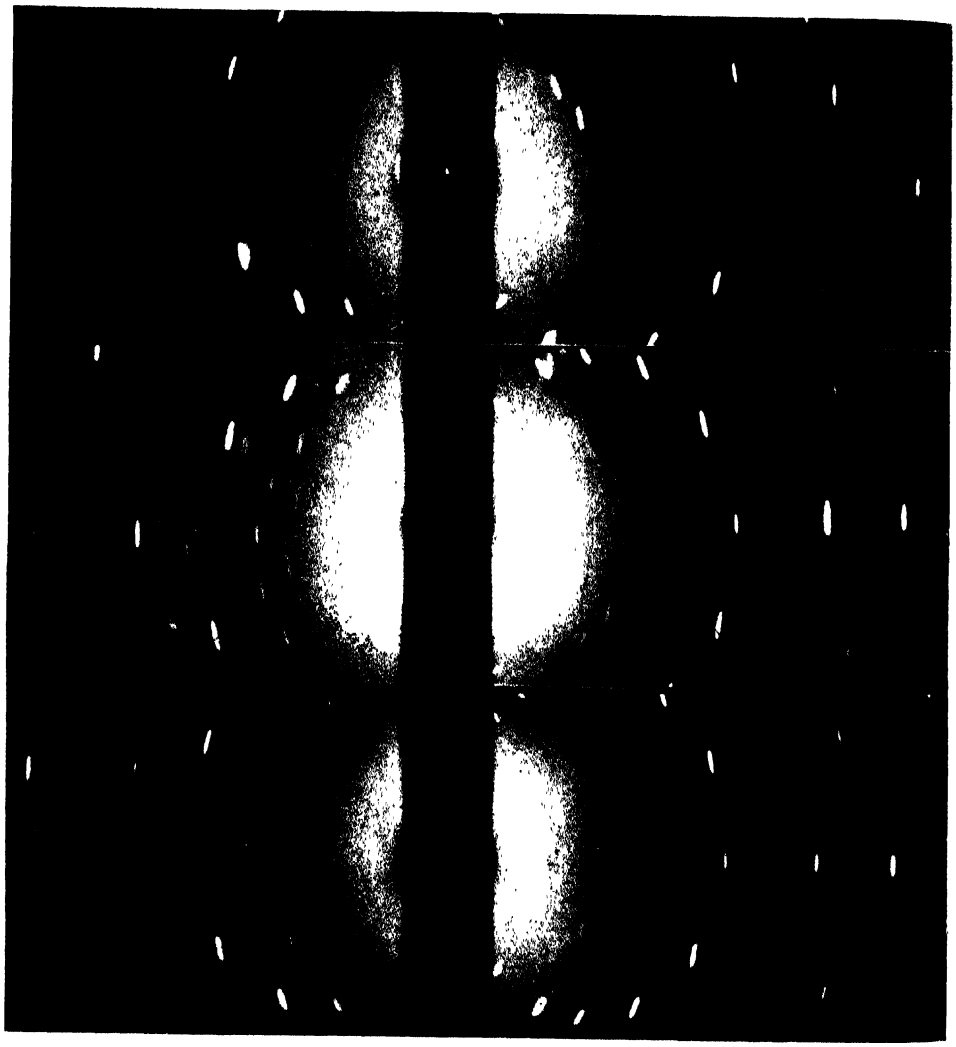
c

Laue photographs showing extra reflections from (211) plane

(*a*) X-ray passes at 18′ to the *b*-axis ; *c*-axis vertical

(*b*) „ „ „ 1°50′ „ „ *b*-axis ; „ „

(*c*) „ „ „ 2°50′ „ „ *b*-axis ; „ „



Laue photographs showing extra reflections from (211) plane

(*d*) Same setting as in (*a*) ; X-ray passes at 3°50′ to the *b*-axis

(*e*) " " " " " ; " " " 5°5′ " " "
extra spot from (321) also appears

(*f*) Same setting as in (*a*) ; X-ray passes at 6°5′ to the *b*-axis,
extra spot from (340)Kα, (340)Kβ also appears.

Anomalous spot (211) (see Plate XIV A-B)

No	Orientation	x	y	h	k	l
a	0°18′	3 15	1 2	2	1.014	1
b	1°50′	3 10	1 2	2	1.0	1
c	2°50′	3 08	1 2	1 95	.9	1
d	3°50′	3.06	1 2	1 95	.87	1
e	5°5′	3.17	1 2	2	.8	1
f	6°5′	3 20	1.2	2	.78	1

The representation of (112) on reciprocal lattice network shows that derangement waves are strictly confined to *b*-axis, such that the disturbance will be more on *b*-axis than on *a*-axis, which is shown on figure 2 (see Datta, 1947).

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